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An On-line Galvanic Cell Generated Electrochemiluminescence and Flow Injection Determination of Calcium in Milk and Vegetable

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Abstract: An on-line Ag/Al galvanic cell is investigated and employed to generate electrochemiluminescence (ECL). The potential of the galvanic cell could be adjusted by varying the components of flow reagent. The cell performed perfect capability of supplying a stable potential for ECL generation. Based on the weak ECL of calcein blue could be greatly sensitized by the presence of calcium in alkaline solution, calcium contents in milk samples and in cabbage were assayed and the results were compared with those from ICP-AES method.

Keywords: On-line galvanic cell, electrochemiluminescence, calcium.

Calcium is an interesting measurand in the field of food science, agriculture and life science[1]. Numerous analysis methods to determine calcium content in different samples have been reported[1-9]. ECL has been proved to be an important and valuable method for analytical applications with increasing interest over the past two decades owing to its high sensitivity and selectivity and simple instrumentation, this also could be seen from the growing number of reviews in this period[10-19]. ECL is also thought to be a suitable method for the detection on microchip[20]. Up to now, the reference technique for ECL generation is carried out by using an external potential supplier. Considering of the size and expense of the potential supplier normally used in research work, it would limit the detection instrumentation miniaturization or even further application of ECL detection on a chip. In this paper, an on line galvanic cell was investigated and applied to the ECL determination of calcium content in milk and vegetable samples. It was found that pure Ag and Al could form a galvanic cell and supply a stable potential in an alkaline solution flow. The potential variation in 1300 mV to 560 mV range could be obtained by varying the concentration of sodium hydroxide or by employing different alkaline buffer flows. Based on above galvanic cell and the enhancement of calcium on ECL of calcein blue, a calcium analysis method is setup to validate the thought of on line galvanic cell generated ECL determination. The manifold of described analysis method is shown in **Figure 1**.

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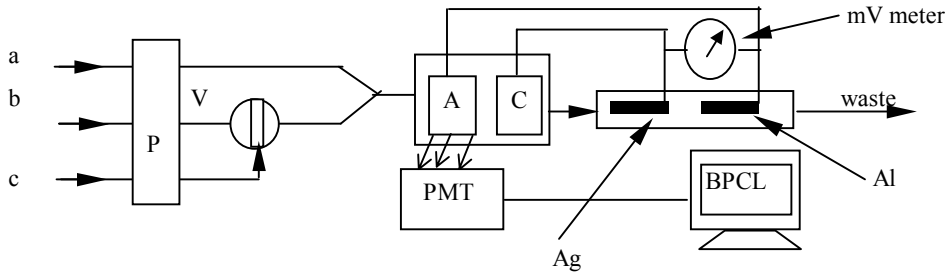
Figure 1 Schematic diagram of experimental apparatus



a: reagent flow of calcein blue and NaOH; b: water; c: sample; P: pump; A: platinum anode; C: platinum cathode; PMT: photomultiplier; BPCL: BPCL ultra-weak luminescence analyzer; V: sixway valve; Ag: silver electrode; Al: aluminum electrode.

Aluminum and silver were found to be the suitable materials to constitute a galvanic cell with low cost. All of the analytical characteristics were considered in detail and optimized as follows: applied potential was 1100 ± 18 mV, reagent and carrier stream flow rate was 100 μL/min, NaOH concentration was 0.18 mol/L, calcein blue concentration was 2.0×10^{-5} mol/L, lifetime of the galvanic cell was more than 200 hours. The potential stability of the described galvanic cell was investigated, experiment results indicated the variety of potential was less than 2%. Possible interference caused by co-existence in milk and cabbage samples was considered as well, experiment results showed ions in pretreated[21] sample solutions did not interfere the determination of calcium.

Under above optimized condition, determination of calcium could be linear in 1.0×10^{-4} mol/L to 8.0×10^{-6} mol/L concentration range and the 3σ detection limit was 2.0×10^{-6} mol/L. The correlation coefficient was 0.999 (n = 7). The relative standard deviation was 3.2% for the determination of 5.0×10^{-5} mol/L calcium standard (n = 9). The calcium contents in four milk products and cabbage bought from local supermarket were determined and the results were compared with those obtained from ICP-AES method as showed in **Table 1**. The calcium recovery experiment results were listed in **Table 2**.

Table 1 Determination of calcium in milk products and cabbage

Sample	proposed method	ICP-AES method[22]	E*%
Milk 1	209 mg/100 mL	200 mg/100 mL	+4.4%
Milk 2	42 mg/100 mL	43 mg/100 mL	-2.4%
Milk 3	25 mg/100 mL	24 mg/100 mL	+4.1%
Milk 4	95 mg/100 mL	90 mg/100 mL	+5.4%
Cabbage (fresh)	220 mg/100 g	221 mg/100 g	-0.5%

All results were means of three analysis
* Relative error

Table 2 The standard recovery test results of calcium in milk products and vegetables ($\times 10^{-5}$ mol/L)

original	add	total	found	recovery (%)
0.92	1.0	1.92	1.90	98
0.92	3.0	3.92	3.94	101
2.19	1.0	3.19	3.2	101
2.19	2.0	4.19	4.2	101
2.19	4.0	6.19	6.28	103
1.70	6.0	7.70	7.48	96

All results were means of three analysis

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